HIGH POLYMERS

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VOLUME V

Cellulose and Cellulose Derivatives

Second Completely Revised and Augmented Edition

Edited by
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Part III

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PART III

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The solvating action of a compound for a polymer may be predicted from Table 2 if several points are kept in mind. First, a crystalline polymer containing largely acidic groups will be soluble primarily in basic solvents, and vice versa. For example, nitrocellulose may be dissolved in solvents containing as active groups all those listed under basic, although most ethers are not good solvents if no other active groups are present. On the other hand, cellulose acetate is soluble in selected solvents containing any one of the listed acidic groups.

Second, the presence of those groups occurring at the top of the columns in Table 2 does not contribute much to the C.E.D. of the polymer, so that a high intensity of solvating action is not necessary if a proper balance of C.E.D. is obtained. An example is ethyl cellulose, which is soluble in a wide variety of solvents drawn from both lists. In some solvents, such as phenols, the ethyl cellulose is certainly solvated. In other solvents, such as benzene, the solubility of ethyl cellulose of high D.S. is undoubtedly due to the good match of C.E.D. and the low tendency for ethyl cellulose to crystallize. Polymers containing groups from the lower portions of either of the columns of Table 2 will have high C.E.D. If the polymer is highly crystalline, a solvent selected from the lower portion of the opposite column will be desirable to solvate the polymer and disrupt the crystal structure. Also, of course, a solvent mixture will have to have the correct C.E.D. to disperse the solvated polymer.

A third obvious point is that polymers containing amphoteric groups or mixed substituents may be solvated by members of either group of solvents.

A fourth and important point is that solvation is not sufficient to ensure solubility. A notable instance is cellulose itself, which is converted by NaOH and other alkalies or by strong acids into crystalline compounds, insoluble in the medium. It is obvious that the solvate, if highly crystalline, will be as resistant to solution as any other crystalline polymer. The maximum solubility of cellulose in NaOH solutions occurs in the concentration range where the extent of reaction is sufficient to weaken the cellulose lattice but not sufficient to transform the structure completely to alkali cellulose.

It is evident from these considerations that the choice of solvent must be such that the original crystal lattice is weakened by solvation, no new stable lattice is created, and the medium as a whole has the correct C.E.D. to dissolve the solvated polymer. In the case of cellulose with strong bases, the hydroxyl ion is the solvating agent. By using a strong organic base with a bulky positive ion, such as tetraethylammonium hydroxide, the

formation of a stable solvate lattice is avoided. Water proves to be a suitable solvent for the solvate produced by the organic bases.

By judicious use of a classification of groups such as given in Table 2 therefore, and a knowledge of a few solvents for a given polymer, it should be possible to predict those potential solvents that are worth trial from a compatibility viewpoint. In addition, some solvents will dissolve because of similarity and not because of solvating tendencies.

7. Hydrogen Bonding

With compounds containing hydroxyl groups, the simple concept of acid–base, or acceptor–donor, interaction does not appear to be adequate to explain solubility behavior. The same is true to some extent for amides and amines insofar as they carry hydrogen on the nitrogen. In all of these cases there is a large tendency for like groups to associate. The usual concept adopted to explain this phenomenon is that the hydrogen in these compounds is nearly a bare, positively charged proton, with no electron cloud preventing close approach of the positively charged proton to a negatively charged atom of another molecule. This close approach results in a high electrostatic energy of interaction of, for example, the hydrogen of one hydroxyl for the oxygen of a second hydroxyl. If steric conditions are suitable, the hydrogen of the second hydroxyl can link to the oxygen of a third hydroxyl, and so on. Alcohols can therefore associate to a considerable extent. The effect is less noticeable with amines, as is indicated by the fact that methylamine boils much lower than methanol.

In the cases of amides and acids, the situation is different in that the active hydrogen of one molecule tends to associate with the carbonyl oxygen of another molecule. This can lead to the formation of a cyclic dimer, and there is little tendency, especially in the case of acids, to form the linear association polymers typical of alcohols. The association of amide and carboxyl groups can also be fitted into the concept of acid–base interaction, the hydrogen being acidic and the carbonyl group basic; accordingly, these groups were included in Table 2. The remaining discussion of hydrogen bonding will be confined largely to the hydroxyl group.

The salient feature of the solubility behavior of compounds containing hydroxyl groups is that they are preferentially soluble in solvents capable of hydrogen bonding. These solvents, which should be considered as a class to themselves, include water, alcohols, phenols, organic acids, amides, and amines. It is found that polymers such as cellulose triacetate and

trinitrate, which contain the typical donor or acceptor groups listed in Table 2 and no hydroxyl groups, dissolve most readily in solvents from the opposite columns of Table 2. Such polymers are insoluble in alcohols. As the hydroxyl content of the polymer increases, however, it becomes increasingly desirable to add alcohols, water, or organic acids to the solvent mixture to promote solubility. Most cellulose derivatives pass through a region of water solubility at a low degree of substitution. Cellulose itself is insoluble in water and other potent hydrogen-bonding solvents only because of its high crystallinity.

Solvation of the hydroxyl groups of cellulose by acids and bases occurs if the concentration is high enough. Cellulose may be dissolved by water solutions of mineral acids and quaternary organic bases, if a concentration range is chosen where a stable, insoluble crystal lattice is not formed.

The hydroxyl group also forms stable complexes with several metallic ions, especially copper. In systems containing cellulose, water, cupric hydroxide, and sodium hydroxide, a new crystalline structure is formed, and the cellulose is more insoluble than in aqueous sodium hydroxide alone. This insolubility is probably due to cross-linking, the copper being coordinated with four hydroxyls, two each from adjoining chains. If either ammonia or ethylenediamine is used instead of sodium hydroxide with the cupric hydroxide, cellulose may be dissolved. The ammonia or the amine competes with the cellulosic hydroxyls for the copper. If correct proportions are used (about 1.9 moles of ethylenediamine per mole of copper), cross-linking is avoided, yet the copper has enough residual affinity to solvate the cellulose and cause solution. With ammonia a wide range in concentration and therefore in base:copper ratio may be employed without difficulty.

8. Variation of Solubility with Substitution

It is evident from the preceding discussion that a solvent can be found for cellulose or for any of its derivatives that are not cross-linked. All that is necessary is that the solvent contain suitable active groups in the correct concentration to solvate the groups on the cellulose chain and that the proper balance of C.E.D. be secured. However, the solutions so obtained may not be very suitable for either technological or scientific use. In the case of cellulose itself, some constituents of the usual solvents are nonvolatile (concentrated hydrochloric acid is an exception). Furthermore, cellulose is highly subject to degradation in its solvents. Frequently it is desirable to alter the infusible, water-sensitive cellulose by introducing

substituents in order to secure a product more suitable for the preparation of protective coatings, films, or plastics. By variation of the nature and amount of substituent groups, both the solubility and the other properties of cellulose may be altered over a wide range. By the use of nonpolar derivatives, such as the ethyl ether or the butyric ester, a relatively soft product soluble in hydrocarbons may be obtained. Derivatives which

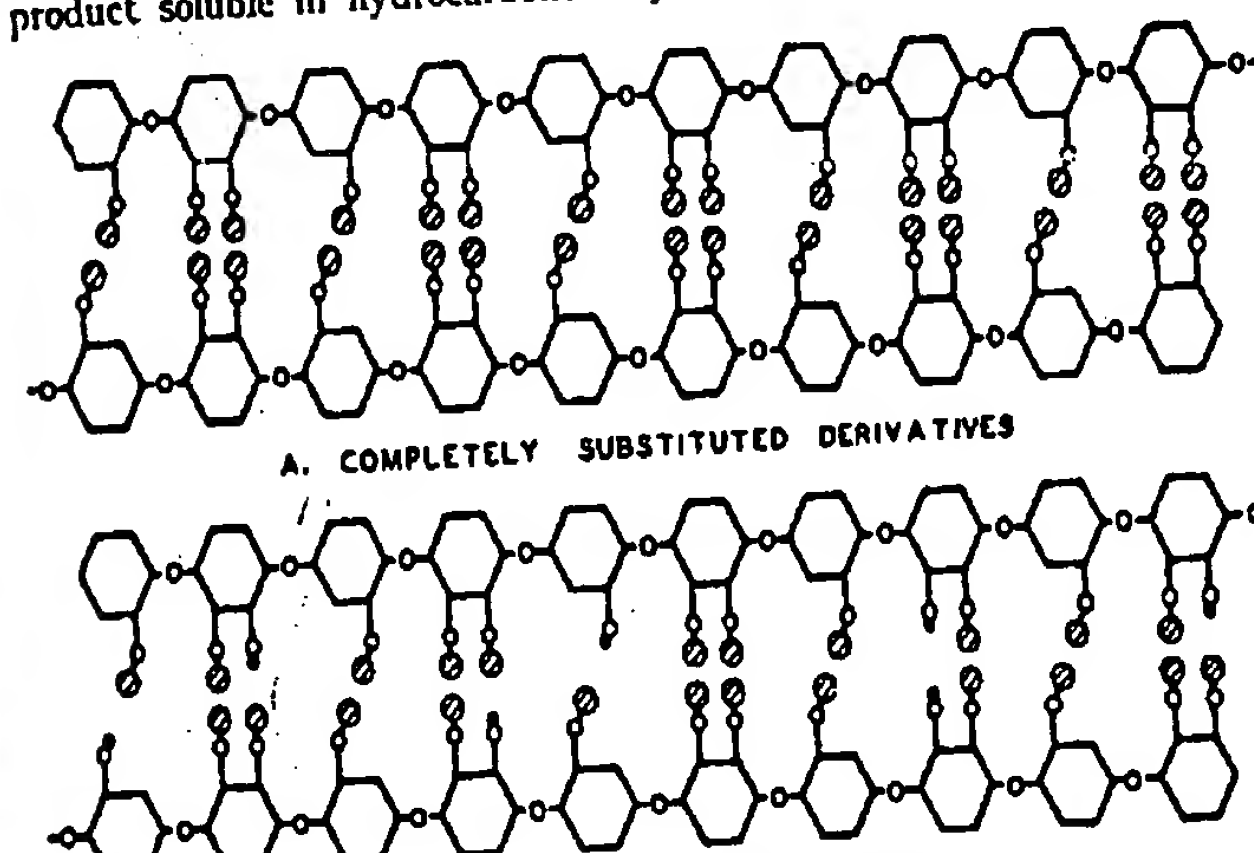

Fig. 6. Area of contact between cellulose chains and effect of substitution. Only substituents between chains are shown; oxygen atoms not shown in rings.
O—Oxygen
●—Hydrogen
⊗—Substituents

are more polar and have little affinity for water, such as the nitrate and acetate, are soluble in polar organic solvents and are hard yet resistant to water.

As the degree of substitution (D.S.) is varied an interesting phenomenon is observed. In all cases, the widest range of solubility is found somewhere between no substitution and complete substitution. Coupled with this effect is the expected trend of solubility with substitution, derivatives of low D.S. being predominantly soluble in water or solvents of high hydroxyl content, and completely substituted derivatives being soluble in nonhydroxylic solvents.

It has long been recognized that the wide range of solubility of incompletely substituted derivatives is caused by the lowered regularity of the

structure. Cellulose itself and the completely substituted derivatives are
easily crystallizable. This shows that the cellulose chains may pack in
such a manner that they fit together easily, giving a large area of contact.
As a few of the relatively bulky substituents are replaced by the smaller
hydroxyl groups, the first effect is to lower the area of contact (Fig. 6).
Also, the hydroxyl groups have relatively low affinity for the usual sub-
stituents. When only a few hydroxyls are present, there is only a slight
chance that two hydroxyls will be opposite each other in adjoining chains.
With lower D.S., the hydroxyl content increases and there is a greater
chance for two hydroxyls to be opposite each other and thus for hydrogen
bonding to occur. With bulky substituents, such as benzyl, several ad-
joining hydroxyls must be unsubstituted before they can approach another
chain closely enough to give strong hydrogen bonding, and the widest
solubility range comes at a lower D.S. than with smaller substituents, such
as ethyl.

The ability to form hydrogen bonds between adjoining chains will,
from probability considerations, increase as the square or a higher power
of the hydroxyl content, and the interruption of the regularity of packing
of initially trisubstituted derivatives will be roughly proportional to the
amount of hydroxyl introduced. These factors act in opposition, the
first hindering and the second promoting solubility. The net result will
be a minimum in the attractive force between chains at some intermediate
value of D.S. With the acetate, nitrate, and ethyl derivatives, this mini-
mum occurs at about D.S. 2.5.

The regularity of packing is also reduced if mixed derivatives of cellulose
are prepared. The mixed acetate-butyrate is therefore somewhat more
soluble than would be anticipated from the progressively increasing solu-
bility of the series cellulose acetate, propionate, and butyrate.

9. Water-Soluble Derivatives

In the same manner that the introduction of a few hydroxyls leads to
higher solubility in organic solvents than is obtained with trisubstituted
derivatives, the introduction of a few substituent groups of almost any
sort reduces the crystallinity of cellulose so that solubility in aqueous media
is greatly increased. A progression of solubility is observed, only a few
tenths of a group per anhydroglucose unit being sufficient to allow solu-
bility in 10% NaOH or 32% HCl. With higher D.S., about 0.5 for car-
boxymethyl cellulose, 1 for ethyl, acetyl, or hydroxyethyl cellulose, or 1.5
for methyl cellulose, true water solubility is reached.

It is impossible to give exact limits for the range of substitution of cellu-
lose ethers that leads to water solubility, because of the well-established
inhomogeneity of substitution of the commercial products of low D.S.
Sometimes this inhomogeneity is intentional, since the resulting thixotropy
and tendency to gelation result in greater thickening power or other useful
properties of the products. An attempt has been made in Table 6 of the
Appendix to give the ranges of substitution for commercial products that
give water or aqueous alkali solubility.

The presence of ionizable substituents such as carboxymethyl or xan-
thate along the cellulose chain promotes water solubility more than does an
equivalent amount of unionized substituent, such as ethyl or hydroxyethyl,
of similar size. This action of ionic substituents is associated with the
repulsive action between chains carrying similar electric charges and with
the large number of particles in the solution, since the freely mobile counter
ions contribute to the entropy of solution. Further information about the
properties of solutions of ionic polymers will be found in Section C of this
Chapter X.

10. Solvents for Cellulose and Its Derivatives

Much factual material on the solubility of individual cellulose derivatives
will be found in Chapter IX and in the Appendix. The solubility of cellu-
lose itself in alkaline media is discussed in Chapter IX-D, and the swelling
of cellulose with water is discussed in Chapter IV-D. There remain some
specific points which are treated here.

(a) CELLULOSE

(1) *Degradation in Solution*

Fibrous, crystalline cellulose is soluble only in the presence of strong
solvating agents. It is an unpleasant fact, from the standpoint of cellu-
lose solubility, that the types of intermolecular forces that lead to solvation
are similar to those responsible for the formation of the intermediate
complexes involved in the catalysis of chemical reactions. As a conse-
quence, cellulose is prone to chemical degradation in solution. In the
case of acidic solvents, the degradation is hydrolytic, and there are no
known means of retarding degradation other than lowering the temperature.
In alkaline solvents, the degradation is oxidative and may be minimized by
absolute exclusion of oxygen and possibly by antioxidants.[22] As the type

[22] H. Staudinger and B. Ritzenthaler, *Ber.*, 68B, 1225 (1935); H. F. Launer and W. K. Wilson, *Anal. Chem.*, 22, 455 (1950).